

Temperature evolution of the structure of liquid 3d transition metals: MD study

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1 INTRODUCTION

One of the major problems in the analysis of diffraction data of disordered systems is the lack of any general method for developing structural models that agree quantitatively with the experimental data. Most analyses are mainly qualitative and are based on a few data features, such as peak positions and coordination numbers derived from radial distribution functions.

Sometimes the results of simulations are in good agreement with experiment (though comparison is made with the radial distribution functions rather than the structure factors), but usually the agreement is only qualitative, and occasionally there are major differences, especially in the descriptions of the liquid state of the 3d transition metals. Usually, the disagreement between model and experimental results is due to the choice of interactive

potentials [1-6]. In this case, the inverse methods [7-12], in which the effective pair potentials are derived from the experimental structural data, is one of the best methods to compute models, structural properties of which quantitatively agree with the experimental data. It is also well recognized that the effective pair potentials estimated from the experimental structural data are quite useful, because they are considered to include, more or less, the particular features of liquid of interest.

The other problem of the simulation the disordered system is the analysis of the obtained information, which represent the complete list of coordinates and velocities of the atoms. Such information allows us to describe the realization of the current state of the system completely. One of the methods of solution of such problems is the statistical analysis of the Voronoy polyhedra built for each atom of the system [13,14] The analysis makes possible the description of the local order of the simulated system.

In the present work the effective pair potentials for liquid 3d transition metals *Fe*, *Co* and *Ni* were derived at the range of temperatures by means of the inverse method proposed in [9] from the experimental structural factors [16]. To test the potentials, the dynamic properties, calculated by means of the molecular dynamics (MD) method, have been compared with their experimental values. Finally, the statistical analysis of Voronoy polyhedra, built on the MD configurations of the investigated metals, has been carried out.

2 METHOD

2.1 THE SELF-CONSISTENT METHOD

The iterative self-consistent method originally proposed by Reatto *et al.* [9] is based on the computer simulations and a formally ex-

act result of the integral equations theory, which relates the effective pair potential with the pair and direct correlation functions $g(r)$ and $c(r)$, respectively:

$$\beta\phi(r) = g(r) - c(r) - 1 - \ln g(r) + B(r), \quad (1)$$

where $\beta = 1/k_bT$, $B(r)$ is so-called *bridge*-function. The functions $g(r)$ and $c(r)$ can be easily obtained from the experimental structural factor $S_{exp}(q)$. However, the *bridge*-function $B(r)$ can not be obtained the same way. This is why in the original Reatto method the *bridge*-function of the hard sphere system $B_{HS}(r, \eta)$, where the external parameter η is the packing factor, was used as an initial estimation for the *bridge*-function, and potential $\varphi_0(r)$ correspondently. As was pointed in the work [9] the convergence of the iterative method depends on the initial approximation of the potential $\varphi_0(r)$. To avoid the dependence on any external parameters in the presented work the mean-field potential $\varphi_{MF}(r)$, which characterizes certain self-consistent field of particles, where the force acting on the particle of the system is the function of all particles arrangement, was used as the initial potential:

$$\varphi_{MF}(r) = -\ln(g(r)).$$

The procedure of deriving effective potential, $\varphi(r)$, is iterative. The equilibrium atomic configuration simulated by means of the molecular dynamics method with given potential $\varphi_i(r)$ corresponds to the pair correlative function $g_i(r)$, direct correlative functions, $c_i(r)$ and structural factor, $S_i(q)$. The next iteration constructs the corrected potential:

$$\beta\varphi(r)_{i+1} = g_{exp}(r) - 1 - c_{exp}(r) - \ln g_{exp}(r) + B_i(r),$$

where the *bridge*-function $B_i(r)$ exactly corresponds to the potential $\varphi_i(r)$:

$$B_i(r) = \beta\varphi_i(r) - g_i(r) + c_i(r) + \ln g_i(r).$$

The iterative process is repeated until the discrepancy χ between the criterion (experimental) and simulated functions becomes smaller than the desired accuracy:

$$\chi = \frac{1}{N} \sum_n^N [g_n^{exp}(r) - g_n^\tau(r)]^2 + \frac{1}{M} \sum_m^M [S_m^{exp}(q) - S_m^\tau(q)]^2, \quad (2)$$

where N and M are the numbers of points in the diagrams of the functions $g(r)$ and $S(q)$.

2.2 COMPUTATIONAL DETAILS

The effective potentials, obtained by means of the inverse method, reproduce the structural properties of the modelled system with good agreement with the experimental data. To check the adequacy of the simulated systems to a real ones it is also necessary to compare the dynamic properties of the system with their experimental values. Therefore, the molecular dynamics (MD) method, which enables the calculation of both structural and dynamic properties of the system, was used in the work presented.

The MD simulations of the $3d$ liquid transition metals have been performed under microcanonical (NVT) ensemble. $N=5000$ spherically symmetric particles, which interact by means of the effective potential $\varphi(r)$, were arranged in a cubic box with the imposed periodical boundary conditions. The size of the box was determined from the condition that the simulated system density is equal to the experimentally measured density of the alloys [15].

The dynamic properties such as self-diffusion coefficient D and shear viscosity η are known to be sensitive to the specified potential of interaction in a system. To investigate the validity of the derived potentials the coefficients D and η have been calculated

by standard Green-Kubo (GK) formulas [17]:

$$D = \frac{1}{3N} \int_0^{+\infty} \sum_i^N \langle v_i(t_0) v_i(t) \rangle dt, \quad (3)$$

$$\eta = \frac{\rho}{k_b T} \int \langle \phi^{\alpha\beta}(t_0) \phi^{\alpha\beta}(t) \rangle dt, \quad (4)$$

where $\alpha\beta=xy, yz, zx$ and $\phi^{\alpha\beta}$ is defined by follow expression:

$$\phi^{\alpha\beta}(t) = \sum_i m_i v_i^\alpha(t) v_i^\beta(t) - \sum_{j>i} (r_{ij}^\alpha) \frac{d\varphi(r_{ij})}{dr_{ij}^\beta},$$

where $v_i(t)$ is the velocity of i -th particle with mass m_i at the time t .

2.3 STATISTICAL ANALYSIS OF THE VORONOI POLYHEDRA

The sensitivity of the statistical analysis of Voronoy polyhedra to the local structure is particularly helpful for understanding the temperature evolution of the structure of disordered systems. The Voronoy polyhedron (VP) is defined as the sub-volume whose interior is closer to a specific atomic vertex than to any other vertex and may provide useful information about the local atomic environment. The most widely applicable forms of the statistical analysis of the VP of disorder systems is the analysis of its metric and topological properties – distribution of VP volumes, face areas, topological indexes etc. However, it is more convenient to perform the analysis by means of the non-dimensional measure – sphericity coefficient K_{sph} :

$$K_{sph} = \frac{36\pi V^2}{S^3}. \quad (5)$$

Here, V is the volume, and S is the surface area of the given polyhedron. Thus, the measure K_{sph} is constructed to be unity

for regular sphere, and defines a deviation of the shape of the given VP from regular sphere. Since each VP is the geometrical image of the local environment of the given atom, the measure K_{sph} will characterize homogeneity of the its local environment. The statistics of the VPs, as the distribution of the sphericity coefficients $N(K_{sph})$, will characterize whole system and for homogeneous systems such distribution must have symmetrical Gauss-like shape.

3 RESULTS AND DISCUSSIONS

In the work the experimental structural factors $S_{exp}(q)$ of liquid iron at $T = 1833, 1873, 1923, 2023$, cobalt at $1823, 1873, 1923, 2023$ and nickel at $1773, 1873, 1923$ and 2023 K [16] were used as the criterion functions for inverse self-consistent method. The obtained effective pair potentials $\varphi(r)$ have reproduced the structural properties of the simulated systems with good agreement to the experimental ones. The deviation χ between simulated and experimental functions reaches only 10^{-4} (fig. 1).

The derived potentials, presented on fig. 2 with the experimental and simulated pair correlation functions, show long-ranged oscillations. For metallic systems such oscillatory behavior is interpreted as the dielectric screening of ions by conducting electrons and can be associated with the Friedel's oscillations.

There is a hump in the main minimum of the effective potentials, which becomes less pronounced with the temperature rise. At motion along the $3d$ row from Fe to Ni the intensity of the hump decreases as well.

It is necessary to note, that position of minimum of the derived potentials r_{min} is shifted with respect to the position of the first maxima of RDFs r_0 . We believe, it can evidence a noticeable con-

tribution of the distant neighbors in the effective interaction. The ratio r_0/r_{min} tends to be unity at high temperatures and at the motion along $3d$ row, that testify that the distant contributions weaken with temperature rise.

To investigate the validity of the derived potentials in the present work the self-diffusion D and shear viscosity η coefficients were calculated for investigated melts. The obtained values are presented on fig. 3 as the function of temperature. There is reasonable agreement between calculated and available experimental and theoretically predicted data [18-29].

Thus, the MD configurations, obtained using the effective potentials, can pretend on the realistic description of the structure of the liquid $3d$ transition metals, since reproduce both structural, and dynamic properties of the melts well.

The distributions of the sphericity coefficient $N(K_{sph})$ were calculated *Fe*, *Co* and *Ni* at different temperatures and presented in fig. 4a, b, c. It is obvious that the shape of the curves $N(K_{sph})$ evolves with the temperature rise. Their maxima are shifted towards the low values of K_{sph} that testify the distortion of the local atomic environment in simulated liquids. At relatively low temperatures the shoulders on the curves were obtained. This fact can be evidence of the existence of some competitive types of the local order. However, with the temperature rise these shoulders disappeared and shape of the distributions $N(K_{sph})$ becomes more symmetrical, which says about more homogeneous structure of the liquid at this temperatures.

To investigate the temperature influence on the local structure of the alloys it is convenient to determine the most probable values of the sphericity coefficient K_{sph}^p , which characterizes the prevailing types of the local order in the structure and establish the dependence of such values on the reduced temperature τ :

$$\tau = \frac{T - T_m}{T_m}, \quad (6)$$

where T_m and T are the melting and current temperatures, respectively.

Fig. 4d demonstrates that at small values of τ the maxima of the curves $N(K_{sph})$ for all simulated metals lie near the value $K_{sph} = 0.7$. We suppose, that this value corresponds to the common symmetry of the local order, which is intrinsic to the dense liquids.

The slope of the dependencies $K_{sph}^p(\tau)$ changes at τ^* , where the distributions $N(K_{sph})$ get more asymmetrical shape. It should note, that at $\tau > \tau^*$ the points of the dependencies for all investigated metals can be approximated by the common linear law (dashed line). The temperature evolution of the distributions $N(K_{sph})$ at $\tau > \tau^*$ allows us to suppose that the differences between the competitive types of the local order in alloys vanish and the structure of liquid becomes more homogenous.

4 CONCLUSIONS

The results of the present work allow us to suppose, that the obtained effective potentials of liquid 3d transition metals at given temperatures can reproduce their real structure, since the model adequately reflect both structural, and dynamic properties of the melts.

The performed statistic analysis of the Voronoy polyhedrons allow us to estimate the temperature range of inhomogeneity $T_m - T^*$ (where $T^* = T_m(\tau^* + 1)$ see fig. 4d). Within of this range metallic liquid contains several competitive types of the local order. Out of this range $T > T^*$ the structure of liquid becomes more homogenous and the character of the local order evolution becomes common for all the investigated metals. According to our estimation, the boundary of the temperature range of inhomo-

geneity is for iron $T^* = 1873\text{ K}$ ($\tau^* = 0.024$), for cobalt $T^* = 1923\text{ K}$ ($\tau^* = 0.061$) and for nickel $T^* = 2023\text{ K}$ ($\tau^* = 0.114$). We believe, that the estimations can be useful on the choice of technological parameters of supercooling of 3d metal-based alloys.

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5 Figure captions

Figure 1. The experimental (open circles) and simulated (solid lines) structural factors $S(q)$ for liquid (a) Fe , (b) Co , (c) Ni at different temperatures. Deviation χ between the functions reaches only 10^{-4} .

Figure 2. The experimental (open circles) and simulated (solid lines) pair correlation functions $g(r)$ with the effective potentials $\varphi(r)$ derived for (a) Fe (b) Co and (c) Ni from the experimental data [16]. The nearest neighbors distance r_0 is shifted with respect to the position of main minimum of the potential r_{min} . Since the ratio r_0/r_{min} tends to be unity at the temperature rising and at the motion along 3d row from Fe to Ni , it means the contributions of the distant neighbors to the effective interaction weaken.

Figure 3. Values of the self-diffusion coefficient D and shear viscosity η (open squares) calculated for the MD configurations of Fe , Co and Ni using the Green-Kubo (GK) relations, and available experimental and calculated data [1, 18-29].

Figure 4. Distributions of the sphericity coefficient $N(K_{sph})$ calculated for liquid (a) iron, (b) cobalt, (c) nickel in the investigated temperature range; (d) The most probable values of the sphericity coefficient K_{sph}^p as the function of the reduced temperature τ . The slope of the dependencies $K_{sph}^p(\tau)$ is changed at τ^* . The behavior of $K_{sph}^p(\tau)$ at $\tau > \tau^*$ can be approximated by linear law (dashed line), which is common for all metals investigated in the present work.







